

## CLAIMS

1. A method of producing hydrogen comprising: providing a steam feed stream, contacting said steam feed stream with a proton conducting membrane supported on a porous redox stable substrate, through said substrate, said membrane being substantially non-permeable to molecular gas and to oxide ions, applying a DC voltage across an anode coupled to the substrate side of said membrane and a cathode coupled to the other side of said membrane so as to dissociate at least part of said steam feed stream therebetween, into protonic hydrogen and oxygen at said anode, allowing said protonic hydrogen to pass through said membrane and form molecular hydrogen at said cathode, and collecting said molecular hydrogen.
2. A method as claimed in claim 1 wherein steam electrolysis is carried out at a temperature of from 400 to 800°C.
3. A steam electrolyser apparatus for producing hydrogen, comprising: a dense proton-conducting membrane substantially non-porous to molecular gas, said membrane being supported on a gas permeable, chemically and mechanically stable, electronically conducting substrate, said membrane being coupled: at the substrate - supported side to an anode for connection to a positive voltage, and to a steam inlet and oxygen outlet for feeding a steam feed stream into said substrate and exhausting oxygen gas released therefrom; and at its other side to a cathode for connection to a negative voltage and a hydrogen gas outlet for exhaustion of hydrogen gas released at said cathode.

4. An apparatus as claimed in claim 3 wherein the substrate material is electrochemically active and the anode constitutes part of the substrate adjoining the membrane.
- 5 5. An apparatus as claimed in claim 3 wherein the anode comprises a thin layer of a different material interposed between the membrane and the substrate support.
6. Apparatus as claimed in any one of claims 3 to 5  
10 wherein the proton conducting membrane is often oxygen deficient perovskite of formula  $ABO_{3-\delta}$  wherein A and B represent metallic elements occupying the A and B sites of the perovskite lattice structure and  $\delta$  represents the degree of oxygen deficiency.
- 15 7. Apparatus as claimed in claim 6 wherein said membrane material is selected from  $BaCe_{0.9}Y_{0.1}O_{2.95}$  (BCY10),  $BaZr_{0.9}Y_{0.1}O_{2.95}$  (BZY) and members of the solid solution,  $BaCe_{0.9-x}Zr_xY_{0.1}O_{2.95}$  (BCZY), or the analogues of the previously mentioned phases  
20 with lanthanides such as Gd, Nd or Yb instead of Y and such phases with higher degrees of substitution such as  $BaCe_{0.8}Y_{0.2}O_{2.95}$  (BCY20),  $Sr_3CaZr_{0.5}Ta_{1.5}O_{8.75}$  (SCZTO) and  $Ba_3Ca_{1.18}Nb_{1.82}O_{8.73}$  (BCN18) composites of such materials.
- 25 8. Apparatus as claimed in any one of claims 3 to 7 wherein the membrane is provided with an outer protective layer.
9. Apparatus as claimed in any one of claim 3 to 8 wherein  
30 the membrane thickness is not more than 25 $\mu$ m.

10. Apparatus as claimed in claim 9 wherein the membrane thickness is from 3 to 15 $\mu$ m.
11. Apparatus as claimed in any one of claims 3 to 10  
5 wherein the membrane comprises a BaZrO<sub>3</sub>-based material.
12. Apparatus as claimed in claim 11 wherein said BaZrO<sub>3</sub> based material is prepared with the use of a sintering aid.
- 10 13. Apparatus as claimed in claim 12 wherein the membrane is of BaZr<sub>1-x</sub>Ln<sub>x</sub>O<sub>3-x/2</sub> wherein X has a value in the range from (0.02) to (0.25) and Ln is a lanthanide ion or La, Y, Sc, and wherein said membrane is produced with the use of approximately 1% w/w of ZnO sintering aid.
- 15 14. Apparatus as claimed in any one of claims 3 to 13, wherein the substrate support is of a material which comprises a metallised ceramic or a mixed conductive oxide, having an electrical conductivity of not less than 10 S cm<sup>-1</sup> at  
20 the operating temperature of the steam electrolysis.
15. Apparatus as claimed in claim 14 wherein said substrate material is selected from Cu:Al<sub>2</sub>O<sub>3</sub>, La<sub>0.8</sub>Sr<sub>0.2</sub>MnO<sub>3</sub> (LSM), chromium-doped LSM (i.e. La<sub>0.75</sub>Sr<sub>0.25</sub>Cr<sub>0.5</sub>Mn<sub>0.5</sub>O<sub>3</sub>) and  
25 La<sub>0.6</sub>Sr<sub>0.4</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-d</sub> (LSCF).
16. Apparatus as claimed in any one of claims 3 to 15 wherein the substrate support pore size is not less than 0.5  $\mu$ m.

17. Apparatus as claimed in any one of claims 3 to 16 wherein the substrate porosity is from 30 to 60%.